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(54) Title: HAIR CONDITIONING SHAMPOO

(57) Abstract

A hair conditioning shampoo in stable emulsion or suspension form comprising: (i) 5 to 40 % by weight of at least one anionic surfactant; (ii) 0.01 to 5 % by weight of a vinyl-type cationic polymer, including a copolymer of acrylamide or a derivative thereof and a dialkyl ($C_1$-$C_5$) diallyl ammonium salt; or a terpolymer of acrylamide, acrylic acid and dialkyl ($C_1$-$C_5$) diallyl ammonium salt; or a copolymer of vinylimidazolium methochloride and vinyl pyrrolidone or mixtures thereof having a hair conditioning effect and a charge density ranging between 150 and 400; (iii) 0.1 to 10 % by weight of at least one dispersed water-insoluble hair conditioning agent; (iv) 0.5 to 10 % by weight of at least one dispersing agent which functions to stabilize the emulsion or suspension; and (v) the remainder water.

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# HAIR CONDITIONING SHAMPOO

## BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to hair conditioning shampoo compositions which are useful to clean human hair while simultaneously conditioning it to render it more easily manageable (combable and relatively low static charge) after shampooing than if it had been washed with a conventional shampoo.

The Prior Art

Hair conditioning shampoos are well known in the cosmetic art and are described in various patents and literature references. Considerable past research underlies efforts to discover new and better conditioning agents for incorporation into hair shampoos to provide so-called "two-in-one" formulations which cleanse the hair as well as provide a hair conditioning effect. These efforts have proved problematic since the combination of hair conditioning agents with the conventional ingredients found in shampoos often results in unstable compositions. The properties of hair conditioning agents and the other ingredients in typical shampoo formulations tend to be mutually antagonistic, rendering the simultaneous washing and conditioning of the hair difficult to achieve. Indeed, the hair-cleansing and hair conditioning properties of these "two-in-one" compositions are usually very inferior to those produced by the utilization of separate shampoo and conditioning formulations.

Among the conditioning agents currently employed in shampoo compositions are silicones and other water-insoluble conditioning agents such as oils, waxes and various polymers. Also utilized are a variety of cationic hair conditioning agents such as cationic quaternary synthetic and cellulose polymers, cationic polysaccharides, etc.

It has been suggested, for example, to employ certain copolymers of acrylamide (or derivatives thereof) and dialkyl diallyl ammonium salts or terpolymers of acrylamide, acrylic acid and dialkyl diallyl ammonium salts as hair conditioning agents in shampoos. Exemplary of such teachings are U.S. Patent Nos. 4,832,872, 4,477,375 and 4,240,450. U.S. Patent Nos. 3,912,808, 3,986,825 and 4,027,008 disclose the use of these and similar polymers to modify the surface characteristics of hair in hair waving and straightening compositions, hair coloring compositions and hair bleaching compositions, respectively.

In U.S. Patent Nos. 4,719,104, 4,954,335 and 4,976,956, the use of certain dialkyl diallyl ammonium chloride polymers in combination with other agents in various hair treating compositions is taught.

Cationic hair-conditioning agents, especially those of mid-to-high charge density, present a particularly difficult problem when incorporated in shampoo compositions since they tend to form complexes with the anionic surfactants normally employed in shampoos. This incompatibility of the differently charged agents would be expected to present serious problems in maintaining the stability of the final product, as well as mutually interfere with the intended action of each.

It is an object of the present invention to provide a novel hair conditioning shampoo containing a unique combination of a mid-to-high charge density cationic hair conditioning polymer and an anionic surfactant, which combination is not subject to the above-noted disadvantages.

## SUMMARY OF THE INVENTION

These and other objects are realized by the present invention which provides a hair conditioning shampoo in stable emulsion or suspension form comprising:

(i) 5 to 40% by weight of at least one anionic surfactant;

(ii) 0.01 to 5% by weight of a vinyl-type cationic polymer, including a copolymer of acrylamide or a derivative thereof and at least 50% of a dialkyl ($C_1$-$C_5$) diallyl ammonium salt monomer; or a terpolymer of acrylamide, acrylic acid and at least 30% of a dialkyl ($C_1$-$C_5$) diallyl ammonium salt monomer; or a copolymer of at least 30% vinyl imidazolium methochloride and vinyl pyrrolidone or

mixtures thereof having a hair conditioning effect and a charge density ranging between 150 and 400;

(iii) 0.1 to 10% by weight of at least one dispersed water-insoluble hair conditioning agent;

(iv) 0.5 to 10% by weight of at least one dispersing agent which functions to stabilize the emulsion or suspension; and

(v) the remainder water.

## DETAILED DESCRIPTION OF THE INVENTION

The invention is predicated on the discovery that certain of the mid-to-high charge density vinyl-type copolymers, such as those copolymers of acrylamide or its derivatives and certain dialkyl diallyl ammonium salts (hereinafter "A-DADAA copolymers") or terpolymers of acrylamide, acrylic acid and dialkyl diallyl ammonium salts (hereinafter "AA-DADAA terpolymers") or copolymers of vinyl imidazolium methochloride and vinyl pyrrolidone, or combinations of these polymers, when incorporated in shampoos with dispersed water-insoluble hair conditioning agents, provide enhanced hair conditioning benefits significantly greater than that provided by other commonly employed "two-in-one" compositions.

The charge density of a cationic polymer is given by the formula:

"Charge Density=Cation Molecular Weight/Number of Positive Charges"

By this definition, a ratio that is lower numerically represents a higher charge density. Thus, the "Charge Density" of a cationic polymer is a numerical value representing the number of positive charges in a particular cationic polymer. The greater the number of positive charges in a cationic polymer of fixed cation molecular weight, the greater will be the "charge density" of the polymer. However, since the charge density, as measured by the above ratio, is inversely proportional to the number of positive charges relative to the cation molecular weight, the greater the number of positive charges and hence the greater the charge density, the lower the numerical value of the above ratio. Thus, for example, a cationic polymer whose charge density as given by the above ratio is 150 will have a "greater" charge density (i.e., greater number of positive charges per unit of cation molecular weight) than a polymer having a measured "charge density" of 200. By "mid charge density" is meant a charge density greater than 200 and less than 400, and by

"high charge density" is meant a charge density ranging between 150 and 200.

It will be understood by those skilled in the art that any vinyl-type cationic polymer having a hair conditioning effect which can be crafted having a charge density ranging between 150 and 400 may be employed in the practice of the invention. Exemplary of such cationic polymers are dimethyldiallyl ammonium chloride/acrylamide copolymer containing at least 50% dimethyldiallyl ammonium chloride monomer (Merquat 280™, which has a charge density of 179.5, and Calgon Corp.'s Merquat 550™, which has a charge density of 232.5); dimethyldiallyl ammonium chloride/acrylic acid/acryamide terpolymers containing at least 30% dimethyldiallyl ammonium chloride monomer (Calgon Corp.'s Merquat 3330™, which has a charge density of 304.5); and vinylimidazolium methochloride/vinyl pyrrolidone copolymers containing at least 30% vinylimidazolium (BASF's Luviquat HM552™, which has a charge density of 255.5). Currently, the preferred cationic polymers are Merquat 550 and Luviquat HM 552.

The dispersing agent and the water-insoluble hair conditioning agent combine to lend stability to the final emulsion or suspension product, as well as lessen the effects of the mutual antagonism between the anionic and cationic components of the composition. The result is a stable "two-in-one" hair conditioning shampoo, wherein the normally incompatible hair cleansing component and conditioning agents can function free of interference from each other to achieve their full effect.

The following $^{14}C$ radiotracer studies using hair and wool swatches as substrates show that Polymer JR 400 (a quaternary ammonium derivative of hydroxyethyl cellulose) and Merquat 550, in the absence of water-insoluble silicone conditioning agents, bind to the same extent on keratin substrates. In the presence of dimethicone in a stable formulation, however, it is found that Polymer JR binding is decreased by 55%, while Merquat 550 binding was unaffected. The reason for this is not fully understood, but is thought to be a function of charge density.

| SHAMPOOS | mg Polyquat/g Hair Swatch | mg Polyquat/g Wool Swatch |
|---|---|---|
| Merquat 550 | 0.086 ± 0.006 | 0.784 ± 0.119 |
| Merquat 550 + Si | 0.069 ± 0.016 | 0.820 ± 0.057 |
| Polymer JR 400 | 0.068 ± 0.045 | 0.758 ± 0.119 |
| Polymer JR 400 + Si | 0.037 ± 0.006 | 0.340 ± 0.039 |

These are surprising and unexpected result since one would expect vinyl-type copolymers (such as Merquat 550) to bind to keratin substrates such as these to about the same extent as other common cationic polymeric hair conditioning agents (such as the cationic cellulosic polymers of the Polymer JR type) and thus would not be expected to provide superior conditioning.

Although the vinyl-type cationic polymers disclosed herein may be incorporated in the aqueous shampoo system in amounts ranging from about 0.01 to about 5% by weight, it is preferred to utilize an amount of such polymers in the range of from about 0.1 to about 2% by weight.

Any anionic surfactant commonly employed in shampoos may be utilized in the practice of the invention.

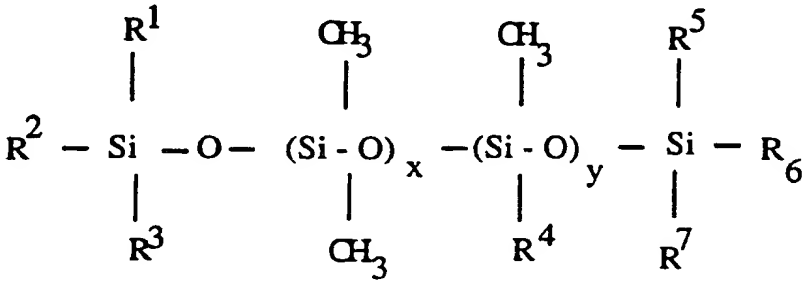
Suitable anionic detergents include those described in McCutcheon's Detergents and Emulsifiers, North American ed., published in 1984. Exemplary of these anionic detergents are alkyl sulfates, alkyl ether sulfates, ethoxylated and propoxylated alkyl ether sulfates containing 1 to 10 ethylene oxide or propylene oxide units per molecule and mixtures thereof wherein said alkyl groups contain 8 to 18 carbon atoms and may be unsaturated, e.g., alkyl ether sulfonates, alpha-olefin sulfonates, alkyl aryl sulfonates or combinations thereof.

Whereas the amount of surfactant incorporated in the shampoo may vary from about 5 to about 40% by weight, it is preferred to employ from about 5 to about 30% by weight thereof.

Any of the well known water-insoluble hair conditioning agents conventionally employed in aqueous shampoos may be used in conjunction with the vinyl-type cationic polymers described above in the practice of the invention. Exemplary of suitable water-insoluble conditioning agents are silicones, aminosilicones,

polyalkylenes and oxidized derivatives thereof, paraffins, petrolatums, microcrystalline waxes, C18-C36 (mixed) fatty acids and mixed triglycerides thereof and stearyl stearates (and other higher esters), as well as mixtures thereof.

The organosilicon compounds and the silicones that may be employed in the practice of the present invention include any of those which are hair conditioning agents intended for use in conditioning shampoos, various of which have been described in the patents mentioned hereinabove. They are preferably of non-volatile types. It has been found that the polyalkyl and/or polyaryl siloxanes are effective, with polydimethyl siloxane (CTFA designation: "dimethicone") being especially preferred. Aminosilicones are also effective conditioning agents in the compositions of this invention, and are even more effective than are conventional silicones and, with respect to these aminosilicones, the present special types described herein are better yet. Thus, it is much preferred to utilize an aminosilicone of the formula:



wherein $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ and $R^7$ are alkyls of 1 to 6 carbon atoms, and most preferably of 1 carbon atom each. $R^4$ is $-R^8-NH-CH_2CH_2-NH_2$, $R^8$ is alkylene of 3 to 6 carbon atoms and most preferably is an isobutyl group, y is an average number in the range of 1 to 10, more preferably less than 5 and most preferably 1, which is of an amine equivalent in the range of 4,000 to 60,000. Preferably, x is in the range of 200 or 300 to 10,000, more preferably 500 to 10,000 and most preferably 750 to 800 or 850, e.g., about 800, and y is in the range of 1 to 10, more preferably being less than 5 and most preferably being about 1. The amine equivalent of such aminosilicone is preferably in the range of 5,000 to 50,000, and more preferably 10,000 to 40,000. For the specific preferred aminosilicone utilized in the experiments reported herein, the molar percentage of amine is about 0.125, the degree of polymerization is about 800, x is

797, y is one and the molecular weight is about 60,000 daltons. Because molecular weights of high polymers sometimes vary, depending on the measurement technique utilized, it is suggested that primary reference should be to the formula for identification of the aminosilicones described, rather than placing primary reliance on the molecular weights provided.

The polyalkylenes that may be employed in the present invention as water-insoluble conditioning agents are preferably those of a molecular weight in the range of 1,000 to 5,000, more preferably 1,000 to 4,000 and most preferably 2,000 to 2,500, e.g., about 2,000. Oxidized versions of these polyalkylene polymers may also be used which create larger hydrocarbons with terminal carboxyl groups. Although the alkylenes of these polymers will usually be ethylene, it is within the scope of the present invention to employ polymers of hydrocarbons of 2 to 5 carbon atoms each, and preferably 2 to 3 carbon atoms, in which the molecular weight range may be from 1,000 to 10,000 or even more under some conditions. Usually, however, the polymers will be of ethylene and/or propylene, and almost always of ethylene.

Paraffins that may be utilized will normally be of chain lengths of 20 to 50 carbon atoms, and preferably 20 to 40 carbon atoms, and isoparaffins can be of chain lengths in the range of 12 to 16 carbon atoms, and preferably 13 to 14 carbon atoms. The petrolatums are petroleum jellies or mineral jellies which melt in the range of 38°C to 60°C and the microcrystalline waxes are of an average molecular weight in the range of about 500 to 800 (which is about twice that of the paraffins). $C_{18-36}$ fatty acid triglycerides are higher triglycerides which are available from Croda Chemical Corporation under the tradename Syncrowax HGL-C. The CTFA designation for this material is C18-36 Acid Triglyceride. Stearyl stearate, which is representative of useful esters of both higher fatty alcohols and higher fatty acids, is available from Inolex Corporation as Lexol SS. This and related compounds such as other high fatty esters may also act as stabilizers for the shampoo composition, preventing settling out of components and phase separations.

Further examples of suitable water-insoluble conditioning agents are set forth in U.S. patent application Serial No. 07/507,335

filed April 9, 1990, and U.S. Patent No. 4,997,641, the entire contents of both being incorporated herein by reference.

Although the water-insoluble conditioning agents can be incorporated in the shampoos of the invention in amounts ranging from about 0.1 to about 10% by weight, it is preferred to utilize from about 0.1 to about 5% by weight thereof.

It is essential to also employ a dispersing agent since many of the shampoo formulations of the invention require it in order to maximize the stability of the emulsion or suspension.

Suitable dispersing agents include long chain saturated primary aliphatic alcohols or derivatives thereof. Additionally useful dispersing agents include long chain acyl derivatives, long chain alkyl dimethyl amine oxides, cross-linked anionic synthetic polymers, polysaccharides or quaternized derivatives thereof.

Suitable long chain primary aliphatic alcohols which may constitute the dispersing agent in the shampoo of the invention are saturated compounds with the hydroxy group being terminally located. Such alcohols will normally be of a distribution of homologous alcohols and typically all are of even numbers of carbon atoms, averaging 24 to 45 carbon atoms (on a weight basis), preferably 28 to 42 carbon atoms, and more preferably about 30 to 40 carbon atoms. When the average number of carbon atoms in the chain is less than 24, the desired effectiveness of such alcohols in the present formulations is decreased, with the stabilization, fiber conditioning and pearlescing actions being diminished. When such chain length is more than 45 carbon atoms, e.g., of an average of about 50 carbon atoms, such alcohols are not satisfactorily dispersible in the described compositions.

In addition to the aforementioned long chain alcohols, related compounds such as corresponding alkoxylated alcohols, corresponding fatty acids and long chain saturated primary alcohol esters may be substituted, at least in part. Of such "derivatives," the alkoxylated alcohols are preferred, and the most preferred of these are the ethoxylated alcohols which will normally contain up to about 20 ethoxy groups per mole, e.g., about 10 to 20. However, the alcohols which are the preferred embodiments of the invention normally will be employed alone or in mixture with related compounds from the "derivatives" group, with the alcohol being the major proportion of the total "alcohol plus derivatives" content.

Examples of commercial materials which may be employed in the present compositions are those manufactured by Petrolite Corporation and sold through their Petrolite Specialty Polymers Group under the name Unilin™ Alcohols as described in the technical bulletin of the Petrolite Corporation entitled Unilin™ Alcohols copyrighted in 1985 and identified as SP-1040. Such alcohols may be 75 to 90%, e.g., 80 to 85%, of the commercial product, with the balance of such products being substantially all saturated hydrocarbons of corresponding chain lengths. In such products, the distribution curve for the alcohol is substantially bell-shaped, with no chain length of alcohol being more than 10% of the total content thereof and with the corresponding hydrocarbon content being of a substantially flat distribution curve, with about 1 or 2% of each of the hydrocarbons being present. Such distribution curves, as bar graphs, are provided in the Petrolite bulletin mentioned above. The alcohols (and corresponding hydrocarbons) present will normally be of chain lengths such that at least 80% are in the range of 18 or 20 to 54 carbon atoms, with at least 80% being in the range of about 18 or 20 to 44 carbon atoms for an alcohol averaging about 30 carbon atoms, and with at least 80% being in the range of about 28 or 30 to 54 carbon atoms when the alcohol averages about 40 carbon atoms. Examples of the long chain primary alcohols are Unilin-425 alcohol which averages 30 carbon atoms in its chain, Unilin-550 alcohol which averages 40 carbon atoms in its chain, and Unilin-350 which averages about 26 carbon atoms in its chain. A derivative, Unithox-550, is an ethoxylated such alcohol having an average of 40 carbon atoms in the alkyl chain, ethoxylated with up to 20 ethoxy groups, e.g., 13.

Suitable long chain acyl derivatives useful as dispersing agents in the shampoos of the invention include those described in U.S. Patent No. 4,741,855, the entire content of which is incorporated herein by reference, e.g., ethylene glycol esters of fatty acids having from about 16 to about 22 carbon atoms. Other acyl derivatives which are useful are alkanolamides of fatty acids having from about 16 to about 22 carbon atoms, preferably about 16 to 18 carbon atoms, e.g., stearic monoethanolamide, stearic diethanolamide, stearic monoisopropanolamide, stearic monoethanolamide stearate, etc. Also useful are long chain esters of long chain fatty acids such as stearyl stearate, cetyl palmitate, etc.; glyceryl esters, e.g., glyceryl distearate;

and long chain esters of long chain alkanolamides, e.g., stearamide DEA distearate, stearamide MEA stearate, etc.

Additionally useful dispersing agents include the alkyl ($C_{16}$-$C_{22}$) dimethyl amine oxides, e.g., stearyl dimethyl amine oxide.

Cross-linked anionic synthetic polymers may also be used as dispersing agents in the practice of the invention. Exemplary of such polymers are polymers of acrylic or methacrylic acid or their derivatives or copolymers with other olefinic comonomers or olefinic compounds with a lipophilic side group or polymers of vinyl sulfonic acid or derivatives or copolymers thereof with other conventional monomers compatible with the objects of the present invention, i.e., polyvinyl sulfate or polystyrene sulfonate.

Useful dispersing agents also include polysaccharides as well as quaternized derivatives thereof, e.g., hydroxyethylcellulose or methylcellulose, guar gum, xanthan gum or quaternary derivatives of the above such as Polymer JR or cationic guar gum.

Also suitable dispersing agents are the alkyl dimethyl amine oxides, the alkyl group having from about 8 to about 18 carbon atoms. Additional suitable dispersing agents are those described in U.S. Patent No. 4,997,641 and U.S. patent application Serial No. 07/507,335 filed April 9, 1990, the entire content and disclosure of each being incorporated herein by reference.

The shampoos herein may also contain a variety of non-essential optional components or adjuvants suitable for rendering such compositions more acceptable to the consumer. These conventional adjuvants are well known to those skilled in the art and include those set forth in the Hartnett Patent No. 4,997,641.

To manufacture the present shampoo, no complex procedures have to be followed, but to obtain best stability, viscosity and appearance, and greatest conditioning activity, it will be desirable to form a dispersion of the water-soluble anionic detergent(s) and adjuvants in water at an elevated temperature such as 70°C to 95°C, melt together and/or dissolve lipophilic materials such as quaternary ammonium salt, hydrocarbons including polyethylene, mineral oil, microcrystalline wax, petrolatum, paraffin and isoparaffin, long chain alcohol and/or "derivative," $C_{18-36}$ fatty acids and/or triglyceride and higher fatty ester, e.g., stearyl stearate, to produce a melt or liquid mix at elevated temperature and admix the two mixes at such elevated temperature, after which heated

silicone and/or aminosilicone may be admixed with the resulting mix (it may sometimes also be included with the lipophiles), with the various mixings taking place with the parts to be mixed being at approximately the same temperature. It is sometimes desirable for the silicone or aminosilicone to be mixed in after the main pre-mixing to promote better stability of the product. When adjuvants are present, those which are water-soluble and/or dispersible may be mixed in with the aqueous phase materials and those which are not water-soluble or dispersible in the aqueous medium may be blended in with the lipophilic materials such as the hydrocarbons, or in some instances may be added to the mixture of the hydrophilic and lipophilic materials either before or after cooling to room temperature. Normally, perfume will be added to the other mixed components after cooling to room temperature, but the silicone and/or aminosilicone will usually be added at elevated temperature and before such cooling. The perfume is added to the cooled composition to avoid losses thereof due to volatilizations of components and to prevent any degradation due to heating it. When the procedure described is not followed, as when the various components of the compositions are blended indiscriminately, less stable products can result which can separate on storage.

All percentages of components expressed herein, unless otherwise indicated, are by weight, based on the weight of the composition in which the component is present.

The invention is illustrated by the following non-limiting examples.

## EXAMPLE 1

The above procedure was utilized to prepare the compositions tabulated below, it being noted that Examples 1-1 and 1-2 are comparative examples:

Formula Examples

| Ingredients | wt % 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Deionized Water | QS | QS | QS | QS | QS | QS | QS |
| Ammonium Lauryl S04 | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 | 15.0 | 7.5 |
| Sodium Deceth-3 Sulfate | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 | --- | 7.5 |
| Cocodiethanolamide | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | --- |
| Cocamidopropyl Betaine | --- | --- | --- | --- | --- | --- | 4.0 |
| Polydimethylsiloxane | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 |
| Polymer JR 400 | 0.3 | --- | --- | --- | --- | --- | --- |
| Polymer JR 30M | --- | 0.3 | --- | --- | --- | --- | --- |
| Guar Hydroxypropyl-trimonium chloride | 0.7 | 0.7 | 0.7 | --- | --- | --- | --- |
| Merquat 550 * | --- | --- | 0.3 | 1.0 | --- | 1.0 | 1.0 |
| Luviquat HM552 ** | --- | --- | --- | --- | 1.0 | --- | --- |
| Distearyldimonium chloride | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| $C_{20-40}$ Alcohol | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 |
| Sodium Dihydrogen Phosphate | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Perfume | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Preservative | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Sodium Cumene Sulfonate | 1.5 | 1.5 | 1.5 | --- | --- | --- | --- |
| TOTAL | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

* cationic copolymer of acrylamide and dimethyl diallyl ammonium chloride

** cationic copolymer of pyrrolidinone and 1-ethenyl-3-methyl-1H-imidazolium chloride

The following lists the above formulas in order of increasing conditioning:

$$1 < 2 < 5 < 3 < 7 < 4 < 6$$

The following comb test was employed to assess the conditioning effects of the various formulations of the examples herein:

Virgin or bleached European hair was made into 3.5 g tresses and washed with 20% sodium lauryl sulfate solution. Each tress was treated with the desired conditioning shampoo for one

minute, then rinsed one minute under running tap water set at 105 F. Three replicates were employed in the test for each shampoo. Panelists were asked to rank the wet tresses in terms of ease of combing and then to assign a rating for each tress on a scale of one to ten, with ten being the easiest to comb. The results were analyzed using the Friedman test for ranking data and Fisher's PLSD method for rating differences at 95% confidence levels.

## EXAMPLE 2

The above procedure was employed to formulate the compositions set forth below, which illustrate the use of various suspending agents:

### Formula Examples

wt % (100% Active)

| Ingredients | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Deionized Water | QS | QS | QS | QS | QS | QS | QS | QS |
| Ammonium Lauryl Sulfate | 7.5 | 10.0 | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 |
| Sodium Deceth-3 Sulfate | 7.5 | 5.0 | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 | 7.5 |
| Cocodiethanolamide | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 |
| Polydimethylsiloxane | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 | --- |
| Polyethylene | --- | --- | --- | --- | --- | --- | --- | 4.0 |
| Merquat 550 | 0.5 | 1.0 | 0.8 | --- | 1.0 | 1.0 | 1.0 | 1.0 |
| Merquat 280 * | --- | --- | 0.2 | --- | --- | --- | --- | --- |
| Merquat Plus 3330 ** | --- | --- | --- | 1.0 | --- | --- | --- | --- |
| Distearyldimonium chloride | 0.5 | 0.5 | 0.5 | 0.5 | --- | 0.5 | 0.5 | 0.5 |
| $C_{20-40}$ Alcohol | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | --- | --- | 3.0 |
| Glycol Stearate | --- | --- | --- | --- | --- | --- | 3.0 | --- |
| Ceteareth-5 | --- | --- | --- | --- | --- | 3.0 | --- | --- |
| Laureth-23 | --- | --- | --- | --- | --- | 1.0 | --- | --- |
| Sodium Dihydrogen Phosphate | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Perfume | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Preservative | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| TOTAL | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

* acrylic acid-dimethyl diallyl ammonium chloride cationic copolymer

** cationic terpolymer of acrylamide, acrylic acid and dimethyl diallyl ammonium chloride

WE CLAIM:

1. A hair conditioning shampoo in stable emulsion or suspension form comprising:

(i) 5 to 40% by weight of at least one anionic surfactant;

(ii) 0.01 to 5% by weight of a vinyl-type cationic polymer having a hair conditioning effect and a charge density ranging between 150 and 400;

(iii) 0.1 to 10% by weight of at least one dispersed water-insoluble hair conditioning agent;

(iv) 0.5 to 10% by weight of at least one dispersing agent which functions to stabilize the emulsion or suspension; and

(v) the remainder water.

2. A hair conditioning shampoo according to claim 1, wherein said vinyl-type polymer is selected from the group consisting of dimethyldiallyl ammonium chloride/acrylamide copolymer containing at least 50% dimethyldiallyl ammonium chloride monomer; dimethyldiallyl ammonium chloride/acrylic acid/acryamide terpolymers containing at least 30% dimethyldiallyl ammonium chloride monomer; and vinylimidazolium methochloride/vinyl pyrrolidone copolymers containing at least 30% vinylimidazolium methochloride.

3. A hair conditioning shampoo according to claim 1 containing 5 to 30% by weight of said surfactant.

4. A hair conditioning shampoo according to claim 1 containing 0.1 to 2% of said cationic copolymer or mixture thereof.

5. A hair conditioning shampoo according to claim 1 containing 0.1 to 5% of said dispersed water-insoluble hair conditioning agent.

6. A hair conditioning shampoo according to claim 1 containing 0.5 to 5% of said dispersing agent.

7. A hair conditioning shampoo according to claim 1 wherein said anionic surfactant is selected from the group consisting of alkyl sulfates, alkyl ether sulfates, ethoxylated and propoxylated alkyl ether sulfates containing 1 to 10 ethylene oxide or propylene oxide units per molecule and mixtures thereof wherein said alkyl groups contain 8 to 18 carbon atoms and may be unsaturated.

8. A hair conditioning shampoo according to claim 1 wherein said cationic copolymer is a copolymer of acrylamide and dimethyl diallyl ammonium chloride.

9. A hair conditioning shampoo according to claim 1 wherein said cationic polymer is a terpolymer of acrylamide, acrylic acid and dimethyl diallyl ammonium chloride.

10. A hair conditioning shampoo according to claim 1 wherein said cationic copolymer is a copolymer of vinylimidazolium methochloride and vinyl pyrrolidone.

11. A hair conditioning shampoo according to claim 1 wherein said water-insoluble hair conditioning agent is selected from the group consisting of silicones, aminosilicones, polyalkylenes and oxidized derivatives thereof, paraffins, petrolatums, microcrystalline waxes, $C_{18-36}$ (mixed) fatty acids and triglycerides thereof and mixtures thereof.

12. A hair conditioning shampoo according to claim 1 wherein said dispersing agent is a long chain saturated primary aliphatic alcohol or a derivative thereof having an average of 24 to 45 carbon atoms in said chain.

13. A hair conditioning shampoo according to claim 10 wherein said dispersing agent is a long chain acylated compound.

14. A hair conditioning shampoo according to claim 1 wherein said dispersing agent is a cross-linked anionic synthetic polymer.

15. A hair conditioning shampoo according to claim 1 wherein said dispersing agent is a polysaccharide or a quaternized derivative thereof.

16. A hair conditioning shampoo according to claim 1 wherein said dispersing agent is an alkyl dimethyl amine oxide.

17. A hair conditioning shampoo according to claim 1 wherein said dispersing agent functions to render said emulsion or dispersion pearlescent.

18. A hair conditioning shampoo according to claim 1 additionally containing shampoo adjuvants.

# INTERNATIONAL SEARCH REPORT

Int. [redacted]l Application No
PCT/US 93/08823

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 A61K7/06 A61K7/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | FR,A,2 585 947 (JOHNSON PRODUCTS CO. INC.) 13 February 1987 see the whole document --- | 1,2,4-7, 10,11 |
| P,X | EP,A,0 522 755 (CALGON CORPORATION) 13 January 1993 see the whole document --- | 1-4,6,7, 9,11, 13-16,18 |
| Y | US,A,4 832 872 (RICHARDSON-VICKS INC.) 23 May 1989 cited in the application see the whole document --- | 1-8,11, 13,16,18 |

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 29 November 1993 | 17.12.93 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax (+31-70) 340-3016 | Sierra Gonzalez, M |

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | PATENT ABSTRACTS OF JAPAN<br>vol. 13, no. 461 (C-645)(3809) 18 October 1989<br>& JP,A,01 180 813 (SHISEIDO) 18 July 1989<br>see abstract<br>----- | 1-8,11,<br>13,16,18 |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 93/08823

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| FR-A-2585947 | 13-02-87 | NONE | |
| EP-A-0522755 | 13-01-93 | AU-A- 1863792 | 07-01-93 |
| | | CA-A- 2072328 | 29-12-92 |
| US-A-4832872 | 23-05-89 | NONE | |